

formed. In one preferred embodiment, the method further comprises removing the exposed coating portion from the substrate comprises contacting the exposed coating portion with a carbon dioxide containing fluid such that the exposed coating portion is removed from the substrate. In

5 another preferred embodiment, the method comprises removing the unexposed coating portion from the substrate comprises contacting the unexposed coating portion with a carbon dioxide containing fluid such that the unexposed coating portion is removed from the substrate.

In one embodiment of the invention, the exposed coating portion has a
10 lower solubility in carbon dioxide relative to the unexposed coating portions. Accordingly, the step of subjecting the coating to a composition comprising carbon dioxide comprises removing the unexposed coating portion from the substrate such that the exposed coating portion remains. Thereafter, the exposed resist can be removed using carbon dioxide as set forth herein.

15 Other embodiments that may be encompassed by the invention include, for example, depositing one or more insulating layers (e.g., interlayer dielectrics (ILDs)) and/or one or more anti-reflective coatings on the substrate. These steps may be carried out in a manner appropriate with the other steps of the process of the invention. The ILDs may be used to keep signals in the
20 microelectronic device from straying between the conducting lines on the chip. Examples of ILDs include, without limitation, materials with low dielectric constants such as SILK resins made commercially available by The Dow Chemical Company of Midland, Michigan (described in detail herein) and Teflon AFTM made commercially available by E.I. DuPont de Nemours of
25 Wilmington, Delaware. Examples of materials for anti-reflective coatings include, without limitation, a fluorinated material based on a fluoroacrylate polymer of polymer precursor.

For the purposes of illustration, an embodiment for illustrating the phase diagram for a negative resist (i.e., base resin) before and after
30 exposure to radiation is set forth in **FIG. 1**. Above each curve, the resin is soluble, below it is insoluble. In accordance with the invention, the resists (e.g., coatings) of the invention can be deposited using carbon dioxide and

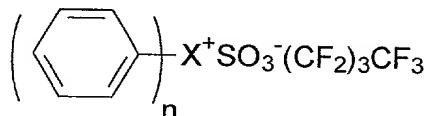
also removed using carbon dioxide such as, for example, by a "stripping" technique. For the purposes of the invention, the term "stripping" refers to the removal of remaining resist from a substrate (e.g., wafer) whether it has been exposed to radiation or not. An example of CO₂ conditions for providing an

5 integrated negative resist system is as follows:

Deposition Density > ρ_1 (e.g., liquid CO₂)
 ρ_1 < Development Density < ρ_2 (e.g., liquid or supercritical CO₂)
10 Removal (e.g., strip) Density > ρ_2 (e.g., liquid or supercritical CO₂)

As alluded to above, carbon dioxide is employed in a liquid or supercritical phase. If liquid CO₂ is used, the temperature employed during the process is preferably below 31°C. As used herein, "supercritical" means
15 that a fluid medium is at a temperature that is sufficiently high that it cannot be liquefied by pressure. The thermodynamic properties of CO₂ are reported in Hyatt, *J. Org. Chem.* **49**: 5097-5101 (1984); therein, it is stated that the critical temperature of CO₂ is about 31°C.

Although not intending to be bound by theory, it is believed that in one
20 embodiment the decrease in solubility in CO₂ of the resist polymer upon exposure to radiation can be achieved by the removal of a blocking group on the polymer which is soluble in carbon dioxide by using a photo acid generator (PAG) that exposes a polar group which renders the polymer insoluble in CO₂. Such an embodiment is illustrated in **FIG. 2**. Examples of
25 PAGs that may be used are numerous and conventionally known in the art including, without limitation, triaryl sulfonium salt, diarylidonium salt, and mixtures thereof. Also, PAGs of the formulas listed hereinbelow can also be used:



30

wherein n is 2 or 3, and X is preferably I or S.

Thus, by manipulating the composition of the polymeric coating (e.g., selecting various polar groups), one can design the polymer such that it is less soluble upon exposure to radiation than the base resin, while allowing the polymer to be dissolved in CO₂ at higher densities and pressures. Thus, one

5 may be able to deposit the polymer using CO₂, develop the negative tone image using CO₂, and remove (e.g., strip) it using CO₂.

In one embodiment, and in accordance with the invention, one is capable of designing the resist such that it can be deposited by utilizing conventional techniques, i.e., known solvents, then developed by employing a

10 first fluid or composition comprising carbon dioxide at a given density, and then stripping the resist using a second fluid or composition comprising carbon dioxide, either in a liquid or supercritical state. The first and second fluids or compositions may be the same or different. Thus, it is believed that the invention is distinguished from U.S. Patent No. 5,665,527 to Allen et al.

15 In another embodiment, the exposed coating portion has a higher solubility in carbon dioxide relative to the unexposed coating portion, and wherein the step of subjecting the coating to a second composition comprising carbon dioxide comprises removing the exposed coating portion from the substrate such that the unexposed coating portion remains. Such an

20 embodiment describes the formation of a positive tone resist, i.e., upon exposure to radiation, the resist becomes more soluble in carbon dioxide. An embodiment illustrating a positive tone resist is set forth in **FIG. 3**. In one example, the CO₂-soluble base resist may have a certain percentage of labile polar groups which, upon exposure to radiation, are removed which enhances

25 the solubility of the exposed coating portion relative to the non-exposed coating portion.

Various polymeric materials may be employed as a coating on the substrate including, without limitation, all of those recited herein. For the purposes of the invention, the term "polymer" encompasses homopolymer,

30 copolymer, terpolymer, and the like. In one embodiment, the component employed in the invention encompasses a polymeric material which is selected from the group consisting of a copolymer of a fluoroacrylate and a